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Composition dependence of elastic constants in wurtzite AlGaInN alloys

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In this paper, we analyze the dependence of elastic constants c_{ij} on composition for random wurtzite quaternary $Al_xGa_yIn_{1-x-y}N$ alloy in the whole concentration range. The study takes as its starting point the c_{ij} parameters for zinc blende phase calculated earlier by the authors on the basis of valence force field model. To obtain the wurtzite constants from cubic material parameters the Martin transformation is used. The deviations from linear Vegard-like dependence of c_{ij} on composition are analyzed and accurate quadratic fits to calculated moduli are presented. The influence of nonlinear internal strain term in the Martin transformation is also investigated. Our general results for quaternary $Al_xGa_yIn_{1-x-y}N$ alloys are compared with the recent *ab initio* calculations for ternaries $Ga_xIn_{1-x}N$ and $Al_xIn_{1-x}N$ (Gorczyca and Łepkowski 2011 *Phys. Rev.* B **83** 203201) and good qualitative agreement is found.

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I. INTRODUCTION

Nitrides are currently the most promising materials for blue, green, and UV optoelectronics. Their applications are diverse and include biosensors, medical imaging, optical data storage, multimedia, etc. One of the important methods of controlling properties of these materials relies on alloying instead of employing pure AlN, GaN, or InN. Modern crystal growth techniques allow for fabricating ternary (e.g., $Ga_xIn_{1-x}N$) and even quaternary $Al_xGa_yIn_{1-x-y}N$ mixtures of these semiconductors. By adjusting the composition, one can tune selected material parameters such as bandgap, lattice constant or polarization to the desired optimal value. It is worth stressing that quaternary alloys, having two compositional degrees of freedom, exhibit much greater tuning potential. In this material, it is possible to control not only the band-gap alone, but also independently another property. Sample application of quaternary alloys' flexibility involve controlling both band-gap and polarization charges, which leads to so-called polarization-matched quantum wells showing very good performance when applied in laser diodes.[1] Therefore, the question about the properties of quaternary alloys is vital. Unfortunately, for these materials not much is known about the exact composition dependence of many properties. Among such quantities are elastic constants. They are very useful when modeling strained alloy layers in quantum heterostructures by means of continuous or coarse grained models (e.g., $\boldsymbol{k}\cdot\boldsymbol{p}$ theory). For sample applications for quaternary $Al_xGa_yIn_{1-x-y}N$, see, e.g., Refs. [2] and [3]. So far, in such modeling, linear dependence of elastic properties on alloy composition was routinely assumed (Vegard-like law). However, there are serious indications that deviations from this simple rule should be expected in the case of elastic properties,[4–7] similarly to, e.g., nonlinear dependence on composition predicted for piezoelectric properties[8]. Since subtle nonlinear effects in elasticity and electrostriction proved to be significant when modeling nitride devices,[9–11] also the accurate composition dependence of c_{ij} can be of interest, for correct and accurate description of nanostructures. In the present study, we give a detailed overview of influence of composition on c_{ij} in random wurtzite $Al_xGa_yIn_{1-x-y}N$. The work is based on our previous calculations for cubic phases.[6] The paper is organized as follows. In Sec. II, we give an overview of the employed methodology and compare the results obtained for binary materials AlN, GaN, and InN with available experimental values. In Sec. III, we present the results obtained for composition dependence of $c_{ij}(x,y)$ in hexagonal $Al_xGa_yIn_{1-x-y}N$ alloys. We also include there a comparison of our results with recent *ab initio* calculations of elastic constants in ternary $Ga_xIn_{1-x}N$ and $Al_xIn_{1-x}N$. Section IV concludes the paper.

II. MARTIN TRANSFORMATION AND ELASTIC CONSTANTS FOR WURTZITE NITRIDES

In our previous work,[6] we calculated the composition dependence of elastic constants in zinc blende $Al_xGa_yIn_{1-x-y}N$ alloys using valence force field (VFF) approach.[12] It is well known that zinc blende and wurtzite structures are closely related. Many semiconducting materials exhibit zinc blende–wurtzite polytypism.[13] Moreover, many properties of the cubic and hexagonal phases resemble each other. In the seventies, Martin derived a transformation between the three independent elastic constants for cubic materials c_{11}^{zb}, c_{12}^{zb}, c_{44}^{zb} and five independent constants of wurtzite c_{11}^{w}, c_{12}^{w}, c_{13}^{w}, c_{33}^{w}, c_{44}^{w}.[14,15] This transformation can be done in two

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steps. In the first stage simple linear relation is employed

$$\begin{pmatrix} c_{11}^{\mathrm{w0}} \\ c_{33}^{\mathrm{w0}} \\ c_{12}^{\mathrm{w0}} \\ c_{13}^{\mathrm{w0}} \\ c_{44}^{\mathrm{w0}} \end{pmatrix} = \frac{1}{6} \begin{pmatrix} 3 & 3 & 6 \\ 2 & 4 & 8 \\ 1 & 5 & -2 \\ 2 & 4 & -4 \\ 2 & -2 & 2 \end{pmatrix} \begin{pmatrix} c_{11}^{\mathrm{zb}} \\ c_{12}^{\mathrm{zb}} \\ c_{44}^{\mathrm{zb}} \end{pmatrix}. \qquad (1)$$

It is already reasonable approximation, however, one can further improve the transformation by adding so called internal strain (IS) nonlinear correction to the Eq. (1). It affects only three coefficients, namely, c_{11}^{w}, c_{12}^{w}, c_{44}^{w}, and the corrected values can be expressed as

$$\begin{pmatrix} c_{11}^{\mathrm{w}} \\ c_{33}^{\mathrm{w}} \\ c_{12}^{\mathrm{w}} \\ c_{13}^{\mathrm{w}} \\ c_{44}^{\mathrm{w}} \end{pmatrix} = \begin{pmatrix} c_{11}^{\mathrm{w0}} \\ c_{33}^{\mathrm{w0}} \\ c_{12}^{\mathrm{w0}} \\ c_{13}^{\mathrm{w0}} \\ c_{44}^{\mathrm{w0}} \end{pmatrix} + \underbrace{\begin{pmatrix} -\Delta^2/c_{44}^{\mathrm{w0}} \\ 0 \\ \Delta^2/c_{44}^{\mathrm{w0}} \\ 0 \\ -\Delta^2/c_{11}^{\mathrm{w0}} \end{pmatrix}}_{\mathbf{IS}}, \qquad (2)$$

where $\Delta = 1/3\sqrt{2}\,[1,-1,-2][\,c_{11},c_{12},c_{44}]^T$, as derived by Martin.[14,15] To benchmark the presented approach for nitrides, we first cross-checked the experimental values for wurtzite binaries AlN, GaN, and InN with those obtained by the above transformation from our theoretical results for zinc blende crystals.[6] The comparison is presented in Table I. Overall the agreement of our prediction with both experimental findings (see Madelung tables[16]) as well as recommended values combined from theory and experiment by Vurgaftman and Meyer[17] is good. One can note that already predictions based solely on Eq. (1) are very reasonable, even when the nonlinear IS term given by Eq. (2) is neglected. The IS correction is the most important for c_{12} constant in examined materials.

TABLE I. Comparison of c_{ij} for AlN, GaN, and InN obtained in this work with experimental values provided in Madelung tables[16] and with recommended values provided in the review paper of Vurgaftman and Meyer.[17]

	c_{11}	c_{12}	c_{13}	c_{33}	c_{44}	
AlN	411	149	99	389	125	experimental values[16]
	396	137	108	373	116	recommended values[17]
	373	119	101	391	108	this work, without IS
	366	126			107	this work, with IS
GaN	377	160	114	209	81	experimental values[16]
	390	145	106	398	105	recommended values[17]
	337	113	97	353	95	this work, without IS
	331	119			94	this work, with IS
InN	190	104	121	182	10	experimental values[16]
	223	115	92	224	48	recommended values[17]
	211	95	86	220	48	this work, without IS
	207	99			47	this work, with IS

III. ELASTIC CONSTANTS IN WURTZITE ALLOYS

After testing the approach on binary materials, we now focus on the case of $\mathrm{Al_xGa_yIn_{1-x-y}N}$ alloys. We apply the Martin transformation to the zinc blende values resulting from our VFF calculations.[6] The elastic constants c_{ij} as functions of AlN and GaN concentrations, x and y respectively, in quaternary $\mathrm{Al_xGa_yIn_{1-x-y}N}$ are displayed in Fig. 1. It turns out that in almost all cases the deviations from linear Vegard-like law are present, similarly to the zinc blende phase. The magnitude of the effect is not very large, reaching its maximum of 4.7% for the c_{44} case. To describe accurately the observed dependencies, one has to add the quadratic bowing contribution $\Delta c_{ij}(x,y)$ to Vegard-like law. The exact functional forms of this term for every considered elastic modulus is depicted in Table II. With this correction the data are reproduced with the accuracy of about 0.2%. One can also notice that $c_{11}(x,y)$, $c_{33}(x,y)$, and $c_{44}(x,y)$ are sublinear. The $c_{12}(x,y)$ is well described by the linear model (Vegard-like law), the maximum observed deviation is 0.2%. This is similar to the case of zinc blende nitride alloys, where all dependencies were sublinear and the c_{12} constant also exhibited the smallest deviation from linearity. In contrast to that, the elastic constant c_{13} exhibits superlinear trend. Such a behavior was not observed for any constant in the zinc blende case. Another interesting issue here is the role of nonlinear IS correction. It turns out that for $\mathrm{Al_xGa_yIn_{1-x-y}N}$ alloys it has the largest influence on $c_{12}(x,y)$ constant. For other constants affected by IS, namely $c_{11}(x,y)$ and $c_{44}(x,y)$, the contribution is lower. In addition, our simulations reveal that IS correction generally decreases slightly the coefficients of bowing function. As a final remark concerning our results for general quaternary $\mathrm{Al_xGa_yIn_{1-x-y}N}$, let us underline that the data for zinc blende nitrides taken as an input to this calculations assume uniform random distribution of cations in the cationic lattice. Therefore, if some kind of clustering occurs in the samples, this effect is not taken into consideration.

Our results could be also compared with recent theoretical findings of Łepkowski and Gorczyca for ternary $\mathrm{Ga_xIn_{1-x}N}$ and $\mathrm{Al_xIn_{1-x}N}$.[7] They carried out their calculations for small wurtzite supercells containing 32 atoms, however, they used very accurate interaction description on the level of quantum mechanical density functional theory (DFT). Interestingly, in order to estimate the influence of clustering, for each composition they computed two configurations — uniform (with In atoms spread evenly throughout the cell) and clustered (where In atoms where arranged close together). For ternary nitride alloys $\mathrm{A}_x\mathrm{B}_{1-x}\mathrm{N}$, the bowing term Δc_{ij} takes on very simple form

$$\Delta c_{ij}(\mathrm{A}_x\mathrm{B}_{1-x}\mathrm{N}) = b\,x(1-x) \qquad (3)$$

having only one parameter b. Therefore, it is natural to use this bowing parameter as a figure of merit for comparison of the two approaches.

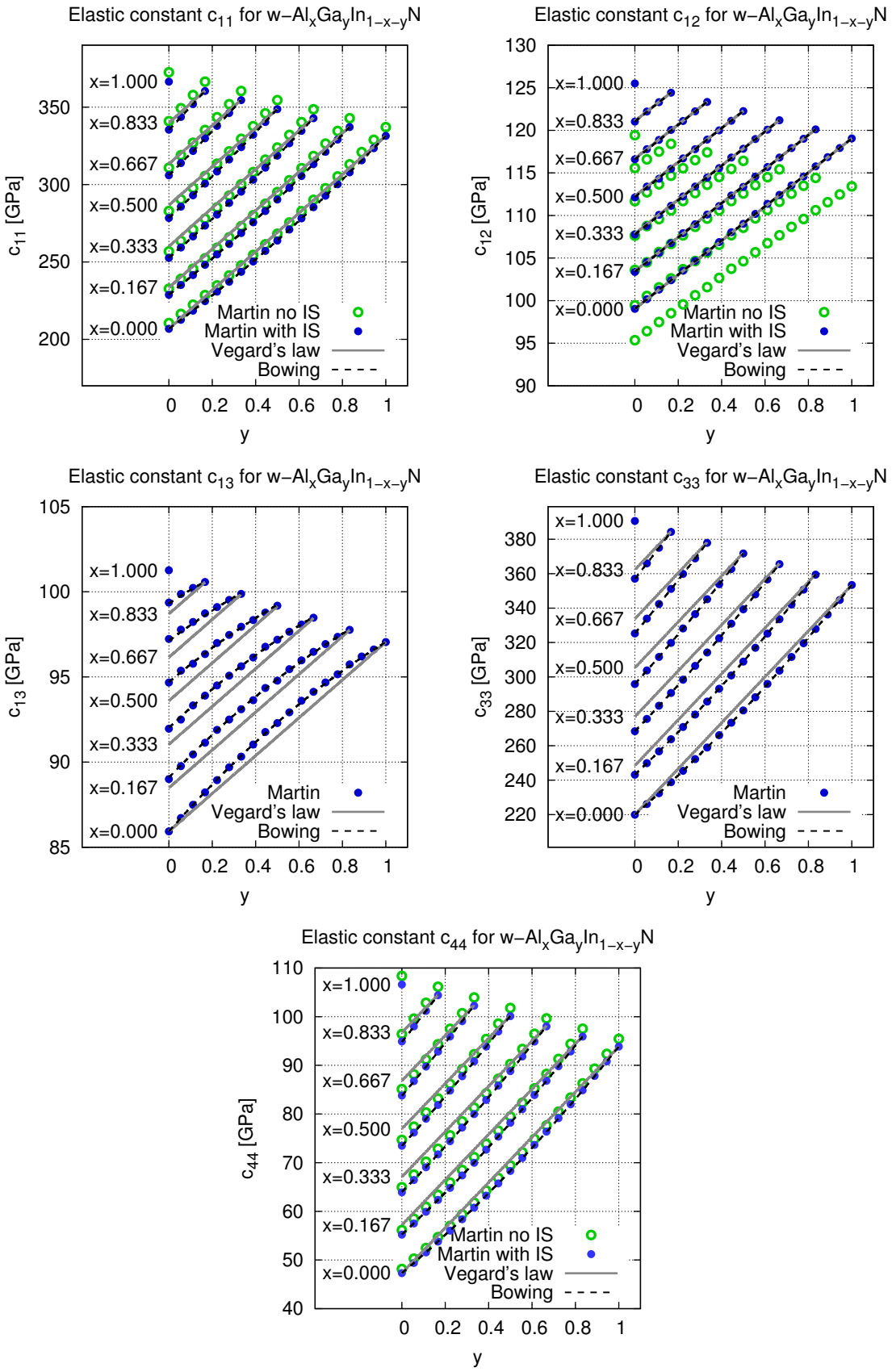

FIG. 1. Dependence of elastic constants c_{ij} on composition for random wurtzite $Al_xGa_yIn_{1-x-y}N$ alloys. For c_{11}, c_{12}, and c_{44}, both the results with internal strain contribution (IS) and without it are presented.

TABLE II. Results of fits to the dependence of elastic constants on composition for wurtzite $Al_xGa_yIn_{1-x-y}N$ alloys.

	Result of fit for c_{ij}	Difference [GPa]
c_{11}	Vegard's law	
	$206.81 + 159.61\,x + 124.63\,y$	8.2 (3%)
	With bowing term Δc_{11}	
	$-32.90\,x(1-x) + 52.97\,xy - 20.89\,y(1-y)$	0.2 (0.1%)
c_{12}	Vegard's law	
	$99.04 + 26.46\,x + 20.00\,y$	0.2 (0.2%)
c_{13}	Vegard's law	
	$85.93 + 15.33\,x + 11.12\,y$	1.2 (1.2%)
	With bowing term Δc_{13}	
	$4.39\,x(1-x) - 7.36\,xy + 3.31\,y(1-y)$	0.2 (0.2%)
c_{33}	Vegard's law	
	$219.93 + 170.74\,x + 133.52\,y$	9.5 (3.2%)
	With bowing term Δc_{33}	
	$-37.73\,x(1-x) + 60.62\,xy - 24.06\,y(1-y)$	0.2 (0.1%)
c_{44}	Vegard's law	
	$47.31 + 59.31\,x + 46.55\,y$	3.5 (4.7%)
	With bowing term Δc_{44}	
	$-13.98\,x(1-x) + 22.79\,xy - 9.06\,y(1-y)$	0.1 (0.1%)

TABLE III. Comparison of results presented in this work with *ab initio* calculation for ternary $Ga_xIn_{1-x}N$ and $Al_xIn_{1-x}N$ obtained in [7].

Bowing	This work	Previous work[7]	
	uniform	uniform	clustered
$Ga_xIn_{1-x}N$			
$b(c_{11})$	-21	-60	-100
$b(c_{12})$	0	-14	-43
$b(c_{13})$	3	4	5
$b(c_{33})$	-24	-71	1
$b(c_{44})$	-9	-16	-35
$Al_xIn_{1-x}N$			
$b(c_{11})$	-33	-80	-141
$b(c_{12})$	0	-9	-47
$b(c_{13})$	4	3	11
$b(c_{33})$	-38	-25	93
$b(c_{44})$	-14	-35	-70

The b values obtained both from our calculations (extracted from Table II) and those provided by Łepkowski and Gorczyca[7] are compared in Table III. Both clustered and uniform cases from Ref. [7] are included for completeness. Our results, however, correspond to the uniform case, since the underlying calculations for zb-$Al_xGa_yIn_{1-x-y}N$ were obtained for even distribution of cations in the sample. It is interesting to notice that, even though the compared results were obtained using very different methods, the qualitative agreement between them is very good. Both approaches predict that significant sublinear behavior can be expected for c_{11}, c_{33}, and c_{44}. The c_{13} is expected to exhibit slight superlinear tendency, whereas c_{12} is the closest to linearity in both models. Generally, the bowing coefficients obtained from *ab initio* calculations[7] are larger than in our VFF model. The change to clustered distribution in the DFT modeling further amplifies the difference. When it comes to the sources of this quantitative disagreement, both approaches carry certain methodological shortcomings — our approach is based on a simple force field, but includes data from large supercell containing over 46 thousand atoms, which diminishes the finite size effects. The approach of Łepkowski and Gorczyca[7] is based on the density functional theory ansatz, so the interactions in that case are described very accurately. However, employed small supercell carries systematic artificial periodicity and implies certain kind of ordering. Interestingly, for the results gathered in Table III, one observes a clear trend — the higher the degree of ordering the larger the magnitude of bowing parameter b. Our results contain the smallest degree of ordering (large random supercell), so the observed b values are the lowest.

IV. SUMMARY

In this paper, the dependence of elastic constants on composition has been studied theoretically for wurtzite random quaternary $Al_xGa_yIn_{1-x-y}N$. It turns out that all $c_{ij}(x,y)$, except for $c_{12}(x,y)$, deviate from the linear dependence on composition, which is commonly employed to estimate elastic properties of alloys. This deviation, however, is not very large, usually around a few percent. We provide accurate quadratic fits to obtained dependencies $c_{ij}(x,y)$ including this bowing effect. Our calculations reveal that for c_{11}, c_{33}, and c_{44} linear model overestimates the calculated moduli. On the other hand, in the case of c_{13} the Vegard-like law leads to underestimation of the material stiffness. The obtained results agree qualitatively with recently published DFT results for elastic constants in ternaries $Ga_xIn_{1-x}N$ and $Al_xIn_{1-x}N$.[7] Even though the described nonlinearities in composition dependence of c_{ij} are not very large, we believe that the awareness of this effect could be useful in modeling nitride heterostructures using continuous or coarse-grained models.

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